These dependences are not allowed for in the simple theory, and so the results in Table VII are necessarily approximate.

Acknowledgment.—I am indebted to Mr. J. Slater of this Department for some of the calculations in Table VII.

ALUMINIZED EXPLOSIVES[1]

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Experimental velocity–diameter $D(d)$ and velocity–density $D(\rho_1)$ curves are presented for 80/20 TNT–Aluminum (Al), 45/30/25 RDX–TNT–Aluminum (Al), 75/25 Composition B–Al (HBX), and various mixtures of ammonium nitrate and aluminum ranging from pure ammonium nitrate to 60% AN. Also presented are some results with AN–DNT mixtures. Results show that aluminum reacts too rapidly for the energy release as a function of time to be a limiting factor in TNT–Al and RDX–TNT–Al mixtures at diameters above 5 cm., but it reacts relatively slowly in the AN–Al mixtures and the rate of reaction of aluminum (and AN), or the rate of energy release is a limiting factor in this case. The familiar properties of the high temperature Al-explosives are here attributed to the thermodynamics of Al-reactions in which the $Al_2O(g)/Al_2O_3(c)$ ratio is appreciable in the detonation wave but becomes negligible later on during adiabatic expansion. The change of this ratio from a high value in the detonation wave to an ultimate low value gives aluminized explosives low "brisance" but high blast potential. The AN–Al mixtures were shown to be "non-ideal" ($D < D^*$) over the entire range of conditions studied. Reaction rates in these mixtures are shown to depend on the particle size of both the AN and the Al. They seem to be controlled by mass transfer which leads to anomalous $D(\rho_1)$ curves each showing a maximum at a relatively low density (1.0 to 1.2 g./cc.).

Introduction

Aluminized explosives are characterized in general by relatively low "brisance" but high (underwater, open air and underground) blast potential. The low relative "brisance" of aluminized explosives has been attributed in the past to incomplete reaction of Al at the "Chapment-Jouguet plane," and the high blast-potential to after-burning of aluminum. Thus early unpublished shaped charge studies with aluminized explosives, interpreted in light of the observed linear variation with detonation pressure of hole depth and volume from jets in uniform targets indicated that aluminum acts effectively as a diluent as far as the end effect, *e.g.*, shaped charge action, is concerned. More careful study showed, however, that aluminum lowers the "detonation" pressure and velocity even more, sometimes quite considerably more, than an ideal diluent. The effectively endothermic reaction of Al in the detonation wave may be seen, for example, in the results of detonation pressure measurements,[2] summarized in Table I, by the shaped charge method (using calibration curves established with known ideal explosives). These data show that the detonation pressures of tritonal and HBX were less than in TNT and composition B, respectively, even though the densities of the former explosives were 6 to 8% higher. This is significant particularly in view of the known pronounced effect of density on pressure. This same situation may also be seen by comparing detonation velocity (Table II), realizing that pressure is given hydrodynamically by the equation $p_2 = \rho_1 DW \doteq \rho_1 D^2/4$. These results show that aluminum lowers the velocity of TNT, 60/40 RDX–TNT and composition B *even more than salt*, sand and similar ingredients which act, if not as pure diluents, at least as (slightly) heat absorbing or endothermic materials.[3] Clearly, therefore, aluminum must have a strongly endothermic effect at the C–J plane. This would be the result, if, for example, $Al_2O(g)$ were to form in appreciable amount in the detonation wave. But if $Al_2O_3(c)$ were the sole aluminum product, the (large diameter) velocity of the TNT–Al and RDX–TNT–Al mixtures would be appreciably higher (even at the same density) than the velocity in the corresponding explosives without aluminum owing to the large heat of formation of $Al_2O_3(c)$.

TABLE I

DETONATION PRESSURES DETERMINED FROM SHAPED CHARGE METHOD

Explosive	ρ_1	Measured detonation pressure p_2(atm. $\times 10^{-3})^a$
TNT	1.59	150
80/20 TNT–Al	1.68	140
TNT	0.81	46
80/20 TNT–Al	0.94	45
Composition B	1.71	230
80/20 Composition B–Al (HBX)	1.81	170
73.2/26.8 Composition B–Al (HBX)	1.83	155

^{a} Average deviation from mean less than 10%.

This article presents experimental studies designed to provide data for the determination of the behavior of aluminum in explosives. Since some theoretical treatments of non-ideal detonation make use of wave shape, measurements of the shapes of the wave fronts of these explosives are also presented.

Experimental

$D(d)$ Curves for Tritonal and HBX.—Velocity–diameter studies of cast and loose-packed 80/20 TNT–Al, cast 75/25 HBX and loose-packed 45/30/25 RDX–TNT–Al are presented in Fig. 1. Velocities were measured by a "pin-

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(1) This investigation was supported by Office of Naval Research, Contract No. N7-onr-45107, Project No. 357,239.

(2) M. A. Cook and A. M. Spencer, "The Determination of Reaction Rates of Non-Ideal Explosives from Shaped Charge Penetration Data," Technical Report XLVII, ERG, University of Utah, August 19, 1955.

(3) M. A. Cook, Paper #25, Discussion of Faraday Society, Physics of High Pressures, Sept. 20, 21, 1956.

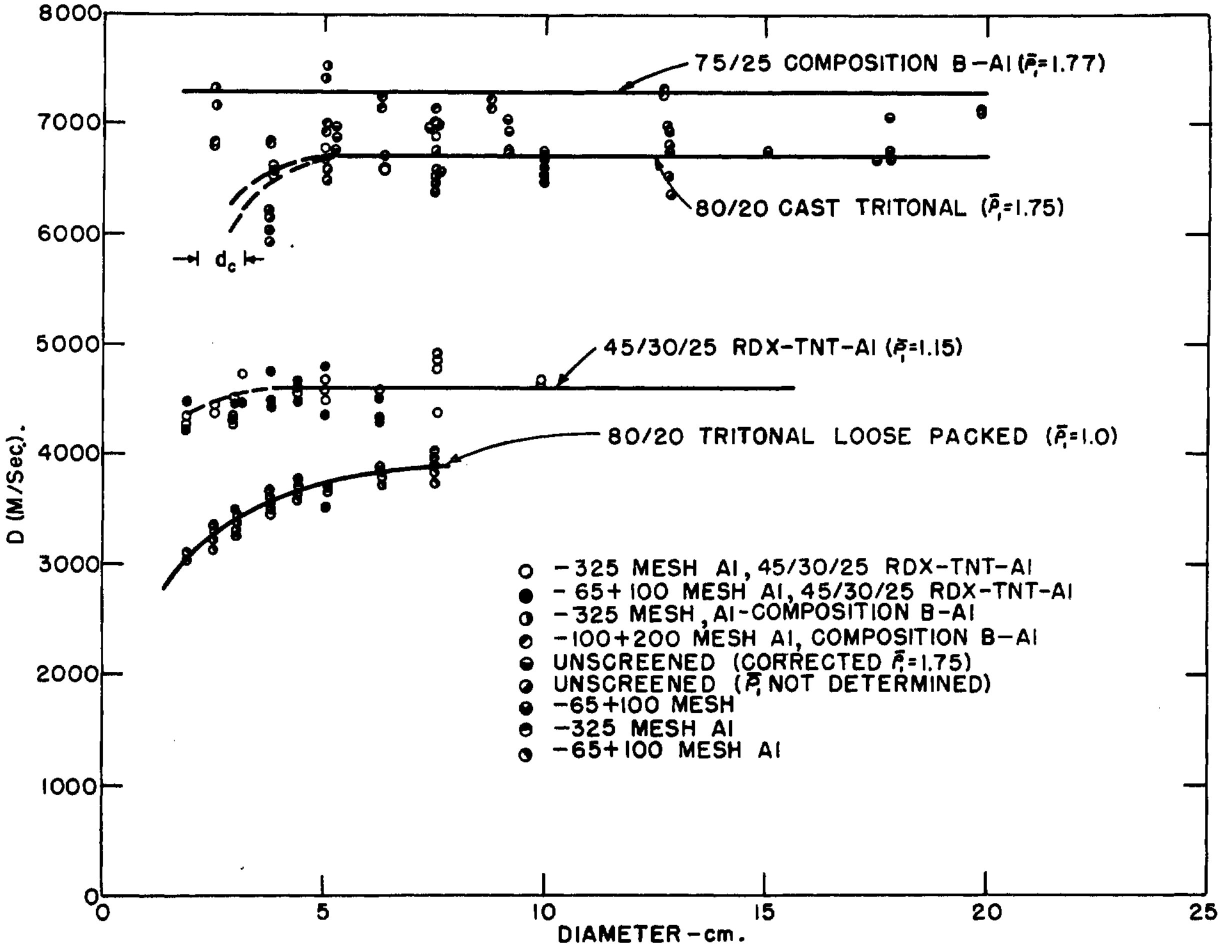

Fig. 1.—Experimental detonation velocity-diameter curves for explosive-metal mixtures.

Table II

Velocity Comparison

Explosive	ρ_1	D(m./sec.)
TNT	1.59	6910
80/20 TNT-Salt	1.75	6900
80/20 TNT-Al	1.75	6800
TNT	0.85	4525
80/20 TNT-Salt	1.00	4400
80/20 TNT-Al	1.00	3840
60/40 RDX-TNT	1.70	7800
45/30/25 RDX-TNT-Salt	1.77	(7430)[a]
45/30/25 RDX-TNT-Al	1.77	7200
60/40 RDX-TNT	1.00	(5650)[a]
45/30/25 RDX-TNT-Salt	1.15	(5400)[a]
45/30/25 RDX-TNT-Al	1.15	4600

[a] By linear interpolation of results for TNT-salt and RDX-salt mixtures.

oscillograph" and by a rotating mirror or "streak" camera as desired. The charges all had a length/diameter (L/d) ratio of six or more. The large diameter charges were contained in thin-walled cardboard tubes and the small diameter ones in thin rolled plastic tubes. Densities were measured in samples of the cast charges by sectioning them. While they were found to show some axial and radial density fluctuations, these variations were limited in all cases to 2% or less. The loose-packed charges were vibrated for density uniformity, care being taken to avoid segregation by excessive vibration. Densities were determined in all cases by total weight/total volume measurements. Velocities were corrected to an average density in each case by appropriate $D(\rho_1)$ relations, only small density corrections being required in any case.

No systematic aluminum particle size or diameter effects were found in either the 80/20 TNT-Al or 45/30/25 RDX-TNT-Al except for the former at diameters less than 5 cm. In fact, in the HBX series no definite influence of diameter on velocity was found in the diameters studied. These results show clearly that the reaction rate of aluminum is not a limiting factor in the behavior of Tritonal and HBX. One must, therefore, look elsewhere for an explanation of low "brisance" in the Al-explosives.

Since theoretical velocity calculations indicated that the $D(\rho_1)$ curve for Tritonal and HBX should not be linear, measurements also were made to determine the velocity-density curves for pressed 80/20 TNT-Al in 8.5 cm. (L/d = 6) charges and for 45/30/25 RDX-TNT-Al at d = 5.2 cm. and L/d = 6. These diameters were chosen to ensure "ideal" detonation. The results are shown in Fig. 2. In accord with predictions, it may be seen that these curves are indeed non-linear; they are quite different from the normal (generally linear) ones. They are evidently characteristic of an $Al_2O(g)/Al_2O_3(c)$ ratio which decreases rapidly with density as discussed below.

$D(d)$ Curves for AN-Al Mixtures.—Experimental $D(d)$ and D vs. per cent. Al (constant ρ_1) data for AN-Al mixtures varying in composition from 100/0 to 70/30 are shown in Figs. 3 and 4. The influence of Al particle size is indicated by some of the results shown in Fig. 3 for 8 to 20% Al. Additional data showing Al particle size effects are given in Tables III and IV. The AN-Al mixtures were all "non-ideal" ($D < D^*$ where D^* is the ideal velocity) at velocities far below the ideal velocities in all cases irrespective of the particle size of either the AN or Al. No attempt was made to correct velocities for small density fluctuations owing to the anomalous $D(\rho_1)$ relations as noted from the data in Fig. 3. For example, the velocity was in general considerably lower on the high density side than on the low density side. Previous unpublished studies have shown that this is

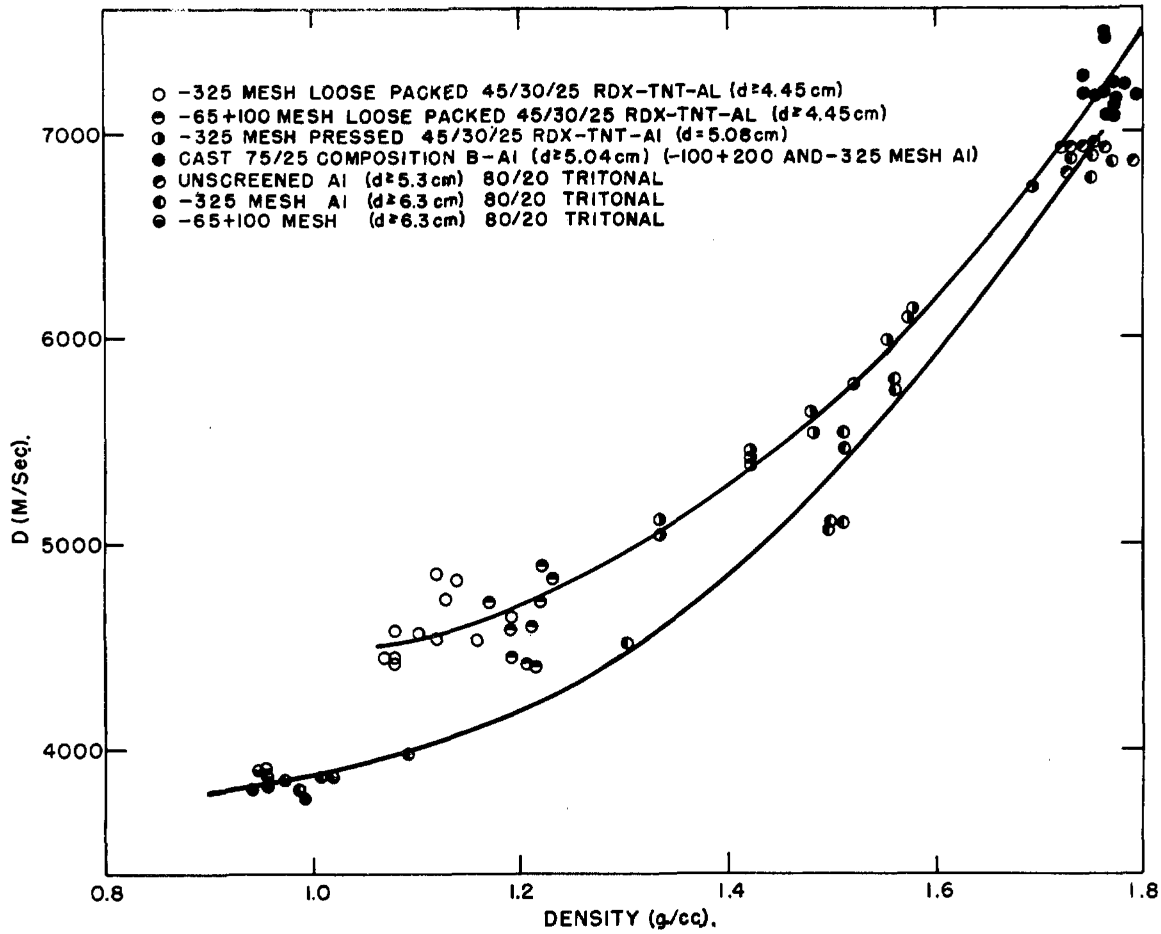

Fig. 2.—Experimental ideal detonation velocity–density curves for 45/30/25 RDX-TNT-AL and 80/20 Tritonal.

a characteristic of fuel or combustible-sensitized AN explosives at D/D^* considerably less than unity.

In order to bring out the anomalous density effect unambiguously, $D(\rho_1)$ measurements were carried out with the 90/10 AN–Al mixture using a single, uniform, unscreened Al sample throughout. These results are shown in Table V. In the first series using a fine AN product (sample 1, Table V) the $D(\rho_1)$ curve was found to go through a maximum between a density of from 1.09 to 1.28. These measurements were repeated about three weeks later using the same lot of AN. However, clearly the sample had changed during the three week interval as a result of partial recrystallization, as observed, for example, by the fact that it then packed to a lower density. In this series the maximum velocity (3485 m./sec.) was observed at about $\rho_1 = 1.12$ and the velocity was 950 m./sec. lower at $\rho_1 = 1.25$ than at $\rho_1 = 1.12$. Pressing crushes the AN somewhat; but to investigate the anomalous $D(\rho_1)$ effect one should use constant particle size. To accomplish this, several shots were made in which the pressed charges were compared with loose-packed ones made by first pressing the AN to the density of the corresponding pressed charge, crumbling the mixture and loose packing it in charges of the same diameter and length. Three comparisons of this sort are shown in Table V (AN samples 3, 4 and 5). Note that the low density product showed a higher velocity than the higher density one, and the difference increased with the density difference. These results show that the $D(\rho_1)$ curve for 90/10 AN–Al with fine AN and fine Al exhibited a maximum at some value of density below $\rho_1 = 1.25$.

A more easily reproducible example of the anomalous $D(\rho_1)$ effect in AN explosive is shown in Table V for a 90/10 AN–DNT mixture using solid DNT and fine AN. Again the $D(\rho_1)$ curve was shown to go through a maximum in this case near $\rho_1 = 1.08$ g./cc.

The AN–Al mixtures are complicated non-ideal explosives; besides the anomalous $D(\rho_1)$ relations, particle size effects may be observed not only in Al but also in AN. The AN particle size was not allowed to vary more than the amount caused by crystal growth in the AN and the inability to reproduce particle size in AN from one lot to another. As a result, no definite particle size effects of AN were noted. To show that the AN particle size also influences velocity in these mixtures, two shots were made in 10 cm. diameter charges using a much coarser AN product and the same grade of aluminum as in the comparative examples. The results (AN sample 6 in Table V) showed an average velocity about 1000 m./sec. lower than for the finer grade AN charges of the same density and Al particle size.

TABLE III

INFLUENCE OF Al PARTICLE SIZE IN AN–Al MIXTURES IN 9.94 (*d*) × 61 (*L*) CM. CHARGES

Al particle size[a]	ρ_1 (g./cc.)	$\bar{D}$ (obsd.) (m./sec.)	Al particle size	$\bar{\rho}_1$ (g./cc.)	$\bar{D}$ (obsd.) (m./sec.)
6% Al			10% Al		
−100 + 150	1.13	Failed	− 65 + 100	1.15	Failed
−150 + 200	1.13	Low	−100 + 200	1.12	3085
−200 + 325	1.14	2495	−200 + 325	1.15	3090
−325	1.20	3050	−325	1.20	3225
15% Al			AN particle size		
− 65 + 100	1.15	Failed	+ 48	13.3%	
−100 + 150	1.14	3170	− 48 + 65	60.2%	
−150 + 200	1.16	2865	− 65 + 100	22.5%	
−200 + 325	1.18	2880	−100 + 150	4.0%	
−325	1.20	2900			

[a] Standard Tyler Mesh.

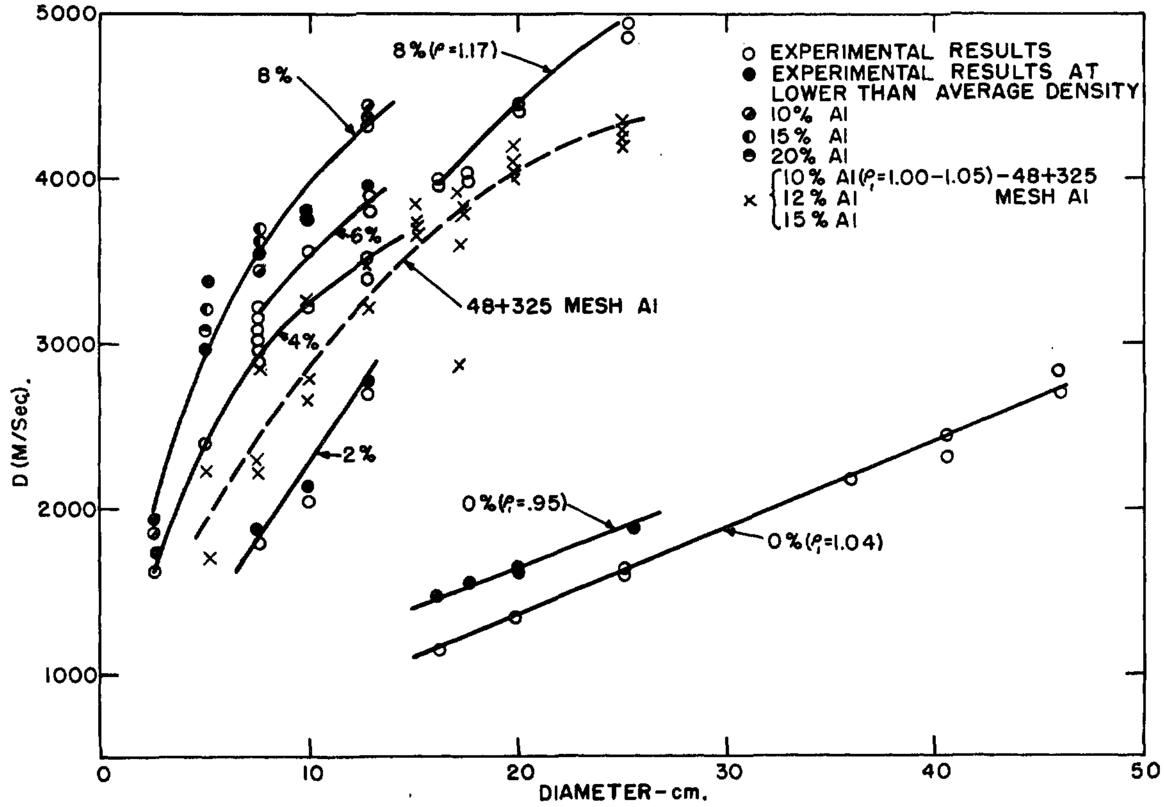

Fig. 3.—Experimental detonation velocity–diameter curves for various AN–Al mixtures.

Table IV

Critical Diameter Data for AN–Al Mixtures

Al, %	Particle size[a]	Critical diameter
0	−325	$12.7 < d_c < 16.0$
2	−325	5.0
4	−325	2.5
6	−325	2.5
8	−325	<2.5
10	−325	2.5
15	−325	2.5
20	−325	$2.5 < d < 5.0$
30	−325	5.0
40	−325	>7.5
10	− 48 + 325	5.0
12	− 48 + 325	$5 < d_c < 75$
15	− 48 + 325	5.0
6	−150 + 200	10.0
10	−100 + 200	10.0
15	− 65 + 100	10.0

[a] AN approximately the same throughout—see Table III.

Table V

Variations of Velocity with Density in AN–Al and AN–DNT Mixtures

90/10 AN–Al (10 × 60 cm.)				90/10 AN–DNT (1) (10 × 60 cm.)			
AN sample	$\bar{\rho}_1$ (g./cc.)	Charge[b]	D (m./sec.)	AN sample	$\bar{\rho}_1$ (g./cc.)	Charge[b]	D (m./sec.)
1[a]	1.07	LP	3280	1	0.88	LP	3310
1	1.09	p	3460	1	.99	LP	3480
1	1.19	p	3410	1	1.08	p	3560
1	1.28	p	3350	1	1.18	p	3330
2	0.96	LP	3365	1	1.27	p	3120
2	1.12	p	3380	7	1.08	p	3315
2	1.17	p	3290	7	1.04	pc	3440
2	1.25	p	2530	7	1.17	p	3210
3	1.07	p	3570	7	1.03	pc	3680
3	0.96	pc	3490	7	1.27	p	2890
4	1.18	p	3405	7	1.07	pc	3700
4	1.00	pc	3715				
5	1.28	p	Failed				
5	0.95	pc	3650				
6	1.12	LP	2595				
6	1.11	LP	2525				

[a] Screen Analysis of samples 1, 6, 7, were

AN Particle Size Data

Mesh	(1)	(6)	(7)
− 10 + 20	..	5.1	..
− 20 + 35	..	70.9	..
− 35 + 48	..	20.2	6.0
− 48 + 65	48.5	2.9	48.4
− 65 + 100	28.5	0.9	36.9
−100 + 150	10.1	..	4.3
−150 + 200	4.8	..	2.0
−200	8.1	..	2.4

Samples 2, 3, 4 and 5 were the same as sample 1 but had aged to 27 days. Aging of AN causes definite changes, the most significant of which is the packing quality. [b] LP = loose packed, p = pressed, pc = pressed and crushed to a loose powder which was then loose-packed. This gave a loose-packed product of the same particle size as in the corresponding pressed charges.

Wave Shape Measurements in Aluminized Explosives.—After considerable effort to obtain quantitative wave shape results in cast Tritonal and HBX, studies were discontinued owing to the very erratic results obtained. The cause of these irreproducible results is associated with the difficulties inherent in casting such mixtures without incurring some density and composition fluctuations; tendency toward segregation of the aluminum causes it to concentrate along the charge axis enough to attenuate the wave at this position more than toward the sides. Only relatively slight segregation of this sort is sufficient to flatten and even in-

TABLE VI

OBSERVED VARIATIONS OF THE STEADY-STATE RADIUS OF CURVATURE/DIAMETER (R_m/d) WITH COMPOSITION AND d IN AN–Al EXPLOSIVES

Al %	d = 2.5 (cm.)	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0	40.0	46.0
				A.	−325 Mesh Al, Fine AN[a]						
0					Failed		1.16	1.09	0.96	0.78	1.03
2		Failed		1.26							
4	Failed	1.33	1.31	1.27	1.31						
6	0.92	1.25	1.55	1.35	1.38						
8	1.35	1.37	1.39	1.39	1.43	1.21	1.31	1.21	1.35		
10		1.68	1.56	1.49	1.39						
15	1.07	1.54									
20	Failed	1.39	1.53								
30		Failed	1.59								
		B. Fine AN, +325 Mesh Al (by removing −325 mesh material from standard[b])									
10		Failed	1.61	1.48	1.50		1.50	1.37	1.67		
12		Failed			1.36	1.29	1.36	(1.26)	1.55		
15		Failed	1.30		1.33	1.63	1.52	1.42	1.45		
				C.	150 to 200 Mesh Al						
6				0.99							
10				1.31							
15				1.30							

[a] AN particle size: + 48 mesh, 0–31%; −48 + 65 mesh, 24–40%; −65 + 100 mesh, 8–40%; −100 + 100 mesh, 4–25%; −150 mesh, negligible. [b] Standard Al particle size: + 65 mesh, 14.9%; −65 + 100 mesh, 13.1%; −100 + 200 mesh, 20.9%; −200 + 325 mesh, 12.7%; −325 mesh, 38.4%.

vert the wave from its normal value for an homogeneous charge. The effect of Al segregation on wave shape is more pronounced than density fluctuations along the charge axis which also tends to flatten or distort the wave.

In loose-packed and pressed charges of 80/20 TNT–Al and 45/30/25 RDX–TNT–Al, the observed wave shapes were obtained with normal reproducibility and showed normal curvature.[4] The waves were spherical in shape and exhibited a normal (constant or steady state) value R_m at large L/d. Values of R_m/d obtained for the loose-packed mixtures of TNT–Al and RDX–TNT–Al with two grades of Al (−325 mesh and −65 + 100 mesh) are plotted against diameter in Fig. 5. R_m/d *vs.* ρ_1 curves for pressed 80/20 TNT–Al and 45/30/25 RDX–TNT–Al obtained at d = 8.3 cm. and d = 5.2 cm., respectively, are also shown in Fig. 5. R_m/d increased for TNT–Al from 1.45 at $\rho_1 = 1.0$ to 2.5 at $\rho_1 = 1.56$ at which density the R_m/d *vs.* ρ_1 curve still had a fairly steep slope. In the RDX–TNT–Al mixture, however, R_m/d increased from 1.95 at $\rho_1 = 1.18$ to an apparent limiting value of about 3.85 at $\rho_1 = 1.48$. This mixture showed no further increase in R_m/d with density as the wave increase from $\rho_1 = 1.48$ to 1.57.

Wave shape data obtained for the AN–Al mixtures are given in Table VI. They show R_m/d to be confined to the relatively narrow range between 0.9 and 1.7 in the diameters studied.

Discussion of Results

At low temperatures and pressures aluminum oxide exists as crystalline Al_2O_3 (corundum), the stable form of which has a heat of formation of 399.1 kcal./mole (using the convention that heat given off is positive). At a pressure of one atmosphere it melts at 2313°K., with a heat of fusion of 26 kcal./mole. The normal boiling point has not been observed directly, but on the basis of experiments made around 2500°K.[5] it has been calculated to be 3770 ± 200°K. Al_2O_3 apparently does not exist in the vapor state; decomposition occurs on vaporization, and apparently the oxide of aluminum in the gas phase consists of AlO.[4] If other materials are present AlO may react with them, and in the presence of reducing mixtures the sub-oxide replaces AlO as the dominant aluminum containing gas. Indirect methods indicate that this sub-oxide is Al_2O.[4] AlO has been studied spectroscopically giving a value for the heat of formation of +45 kcal./mole. However it is pointed out in reference 5 that the lower electronic state found in the spectroscopic studies may not be the ground state of the molecule. Chemical evidence is presented there which indicates a heat of formation of about −8 kcal./mole for AlO. Reference 5 gives results which indicate a heat of formation for Al_2O of about 39 kcal./mole.

The only compounds of aluminum which might conceivably form in detonation besides the oxides are AlN and AlH. Al_4C_3 exists only in the solid state, decomposing on vaporization. However, careful considerations show that none of these can be important as detonation products and the significant products are considered therefore to be only Al_2O_3(c), Al_2O(g) and AlO(g).

The heat capacities at constant volume for Al_2O and AlO were calculated on the basis of rigid-rotor and harmonic-oscillator approximations. The spectroscopically observed frequency of 977 cm.$^{-1}$ was used for AlO. For Al_2O no data were available. Comparing with other triatomic molecules, and assuming that Al_2O is non-linear, it was assumed that Al_2O has vibration frequencies of 500, 977 and 1580 cm.$^{-1}$. The harmonic oscillator heat capacities were taken from a table given by Aston.[6] Heat capacity data for Al_2O_3 are given by Ginnings and Corruccini up to 900°.[7] The reactions yielding Al_2O(g) and AlO(g) may be reduced to

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(4) M. A. Cook, G. S. Horsley, R. T. Keyes, W. S. Partridge and W. O. Ursenbach, *J. App. Phys.*, **27**, 269 (1956).

(5) L. Brewer and A. W. Searcy, *J. Am. Chem. Soc.*, **73**, 5308 (1951).

(6) H. S. Taylor–S. Glasstone "Treatise on Physical Chemistry," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1942, Appendix I.

(7) D. C. Ginnings and R. J. Corruccini, Paper 1797, *J. Research Natl. Bur. Standards*, **30**, 593 (1947).

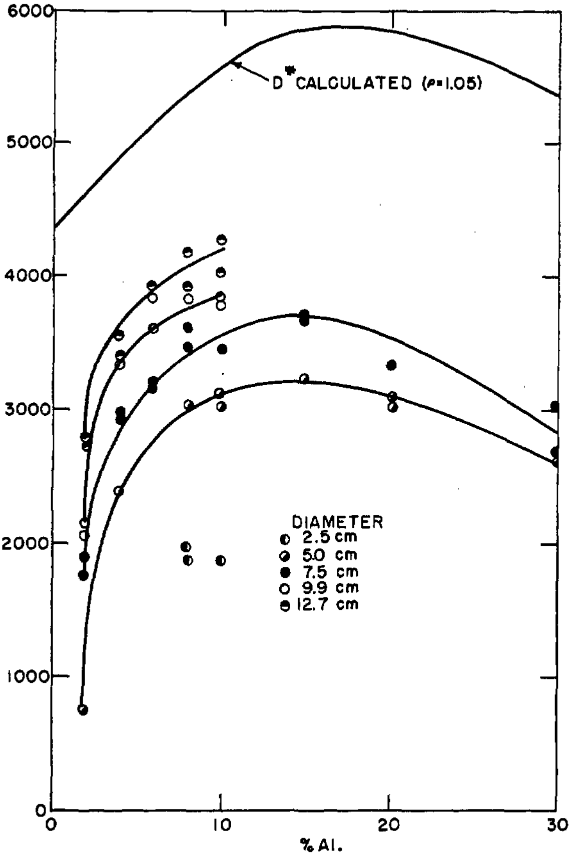

Fig. 4.—Detonation velocity *vs.* per cent. aluminum curves for AN–Al mixtures.

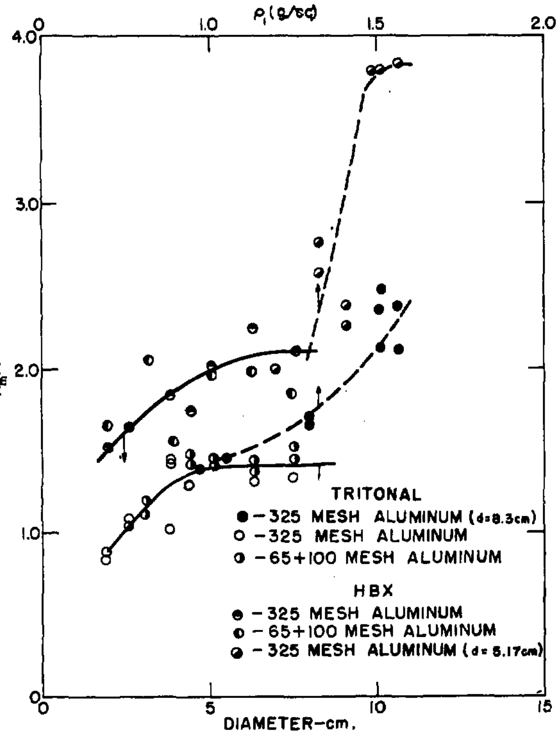

Fig. 5.—R_m/d (steady-state radius of curvature/charge diameter) *vs.* charge diameter and density for 80/20 TNT–Al and 45/30/25 RDX–TNT–Al.

$$Al_2O + 2CO_2 \rightleftarrows Al_2O_3 + 2CO$$
$$AlO + {}^1/_2CO_2 \rightleftarrows {}^1/_2Al_2O_3 + {}^1/_2CO$$

Their equilibrium constants (using definitions published elsewhere) are[8]

$$K_{p28} = \frac{f_{Al_2O}f^2_{CO_2}}{f^2_{CO_2}}\,;\ K_{28} = K_{p28}\left(\frac{1.2181}{T}\right) = \frac{(Al_2O)(CO_2)^2}{(CO)^2}\,F$$

$$K_{p29} = \frac{f_{AlO}f_{CO_2}{}^{1/2}}{f_{CO}{}^{1/2}};\ K_{29} = \left(\frac{1.2181}{T}\right)K_{p29} = \frac{(AlO)(CO_2)^{1/2}}{(CO)^{1/2}}\,F$$

(Definition of F given by equation 12, reference 8.) Solving these expressions for (Al_2O) and (AlO)

$$y_{22} = (Al_2O) = K_{28}\,\frac{(CO)^2}{(CO_2)^2}\,\frac{1}{F}$$

$$y_{23} = (AlO) = K_{29}\,\frac{(CO)^{1/2}}{(CO_2)^{1/2}}\,\frac{1}{F}$$

Putting the remaining aluminum into Al_2O_3 one finds

$$y_{24} = (Al_2O_3) = {}^1/_2Al_0 - y_{22} - {}^1/_2y_{23}$$

where Al_0 is the number of gram-atoms of Al in 100 grams of explosive. (Designations here adopted conform to extensive tabulations and conventions using derivations previously published.[8])

There is sufficient uncertainty in the available thermochemical data for Al_2O and AlO that a considerable variation is possible in the values of the equilibrium constants calculated by statistical mechanics. While it does not, therefore, seem possible at the present time to give precise values for the K_p, the following are considered to be the best data available at present

$$K_{p28} = 10^{21.4}10^{-63,200/T}$$
$$K_{p29} = 10^{13.3}10^{-49,000/T}$$

Heat capacity data computed by the approximate methods outlined above are given in Table VII. With these data one may carry out at least qualitative thermo-hydrodynamic calculations for aluminized explosives.

Temperatures and pressures at the C–J plane for low density TNT–Al and RDX–TNT–Al mixtures are according to calculations based on the above data such that the chief product of aluminum should be $Al_2O(g)$. This forms endothermically with respect to the products of detonation of these explosives, (*i.e.*, by removing oxygen from more exothermic reactions) and as a result the intensity of the detonation wave is reduced by aluminum. Owing to the much more rapid increase of pressure than temperature with density, however, the ratio $Al_2O(g)/Al_2O_3(c)$ should decrease with density, but evidently remains appreciable even at the maximum density possible. As a result the influence of the highly exothermic product $Al_2O_3(s)$ apparently never is sufficient in Tritonal and HBX to overcome the endothermic effect at $Al_2O(g)$ at the C–J plane. The detonation velocities and detonation pressures (or "brisance") of these high temperature aluminized explosives are thus always lower than those of the corresponding explosives without aluminum even at the maximum densities, despite a 6 to 8%

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[8] M. A. Cook, R. T. Keyes, G. S. Horsley and A. S. Filler, This Journal, **58**, 1114 (1954). See also M. A. Cook, *J. Chem. Phys.*, **16**, 1081 (1948).

TABLE VII

IDEAL MOLAL HEAT CAPACITIES FOR ALUMINUM OXIDES

	$\overline{Cv}$			Cv		
T, °K.	Al_2O_3(c)	AlO(g)	Al_2O(g)	Al_2O_3(c)	AlO(g)	Al_2O(g)
1000	26.67	6.22	9.69	27.89	6.658	10.868
1100	27.10	6.28	9.84	30.32	6.705	11.024
1200	27.48	6.33	9.98	30.70	6.743	11.150
1300	27.82	6.37	10.10	31.02	6.772	11.252
1400	28.13	6.41	10.21	31.34	6.800	11.339
1500	28.40	6.44	10.31	31.60	6.816	11.405
1600	28.66	6.47	10.40	31.83	6.832	11.463
1700	28.89	6.50	10.47	32.06	6.845	11.512
1800	29.11	6.52	10.54	32.28	6.857	11.553
1900	29.32	6.54	10.61	32.48	6.867	11.589
2000	29.51	6.56	10.67	32.66	6.875	11.620
2100	29.69	6.58	10.72	32.80	6.885	11.649
2200	29.86	6.60	10.77	32.92	6.889	11.670
2300	30.01	6.61	10.82	33.05	6.894	11.690
2400	30.16	6.63	10.86	33.15	6.899	11.709
2500	30.30	6.64	10.90	33.23	6.903	11.724
2750	30.59	6.67	10.98	33.41	6.912	11.757
3000	30.85	6.69	11.06	33.55	6.919	11.783
3250	31.09	6.71	11.12	33.67	6.924	11.804
3500	31.29	6.73	11.17	33.74	6.928	11.820
3750	31.47	6.74	11.22	33.79	6.932	11.833
4000	31.63	6.75	11.26	33.83	6.934	11.843
4250	31.77	6.76	11.30	33.85	6.937	11.852
4500	31.89	6.77	11.33	33.87	6.939	11.860
4750	32.01	6.78	11.36	33.89	6.940	11.866
5000	32.11	6.79	11.39	33.90	6.942	11.873
5250	32.20	6.80	11.41	33.91	6.943	11.878
5500	32.28	6.81	11.44	33.92	6.944	11.882
5750	32.36	6.81	11.46	33.93	6.945	11.886
6000	32.43	6.82	11.48	33.94	6.946	11.889

higher density for the aluminized explosive. Compare, for example, Fig. 2 with the experimental $D(\rho_1)$ curves for TNT and RDX, namely

$$D = 5900 + 3650(\rho_1 - 1.0) \quad \text{(RDX)}$$
$$D = 5010 + 3225(\rho_1 - 1.0) \quad \text{(TNT)}$$

See also Tables I and II.

The ratio $Al_2O(g)/Al_2O_3(c)$ falls to zero at temperatures below about 3500°K. at the "explosion pressures" p_3 of the high density aluminized explosives, or below about 3000°K. at very low densities. (The "explosion" state here follows the usage of Schmidt.[9] The subscript 3 refers to the initial conditions of the real work process corresponding to the gaseous products at the same density as the original explosive, and subscript 4 to the final state of the work integral. This quite correctly ignores the influence of the detonation wave since this wave has only a transient influence compensated by the rarefaction wave as far as the work integral A is concerned). This apparently causes the temperature to be buffered at a value between 3000 and 3500°K. during adiabatic expansion. The maximum available energy or total blast potential is determined by the work integral

$$A = \int_{v_3}^{v_4} p\mathrm{d}v = Q - q$$

where A is the maximum available work in adiabatic expansion of the products of detonation from specific volume v_3 to v_4, Q is the heat of explosion and q is the heat retained by the products of detonation at v_4. In general, explosives are very efficient in utilizing Q in work processes as long as the confinement of the burden is adequate. In open air blasts the compressibility of air is such that A/Q is only about 0.15 to 0.2, but in underground and underwater blasting A/Q −0.8 to 1.0 depending primarily on ρ_1. In either case, however, the buffering action of the ratio $Al_2O(g)/Al_2O_3(c)$ on temperature will tend to increase Q and A in aluminized explosive approaching as far as the maximum available energy is concerned, the high value corresponding to zero in this ratio. Only where v_4 is effectively only slightly greater than v_3, as in applications requiring high brisance (*e.g.*, end effect phenomena including impulsive loading of targets, cavity effect, etc.) will the high $Al_2O(g)/Al_2O_3(c)$ ratios applicable in the wave front of detonation be important in lowering intensity. In cases where v_4 is much greater than v_3, this ratio should be effectively zero. The thermodynamics of the $Al_2O(g)/Al_2O_3(c)$ ratio thus appears to give a satisfactory explanation of the behavior of the important high temperature, aluminized explosives. Quantitative computations accurate within the accuracy of the thermodynamic data presented above are possible for any particular set of conditions.

The situation is somewhat different in AN–Al mixtures. In the first place these mixtures have low enough detonation temperature and sufficient oxygen at Al < 15% that $Al_2O(g)/Al_2O_3(c)$ ratio is practically zero in this range. At 20% Al, where the explosive is approximately oxygen balanced, this ratio is still quite low and Q for detonation conditions is a maximum (at 1355 kcal./kg.) since the ratio $Al_2O(g)/Al_2O_3(c)$ increases rapidly as Al is further increased owing to the rapidly increasing temperature. However, in work processes where v_4 is effectively much greater than v_3, A should continue to increase with per cent. aluminum in the AN–Al mixtures, perhaps to as high as 35 to 40% Al. The AN–Al explosives in this composition range should thus be very powerful ones for underwater, air-blast and underground use. However, while they should develop sustained pressures, their peak pressures under all circumstances will be very low, particularly in small sizes where $D/D^* << 1$.

Finally, let us consider some aspects of the kinetics of the reactions of AN–Al and AN–DNT mixtures in detonation. In previous studies of nonideal explosives, including both pure explosives and mixtures, the surface burning (two-thirds order) rate law described by Eyring, *et al.*,[10] was found to apply. The explosive mixtures studied, however, were of a type in which the temperature generated by the reaction of at least one of the ingredients alone without mixing with those of any of the other components would raise the temperature in the products to or above the final equilibrium T_2. In AN–Al mixtures, on the other hand, the temperature attained by reaction of AN alone cannot exceed about 1700°K., whereas that for the complete mixtures goes much higher. Hence mass transfer and possibly heat transfer are much more important factors in these mixtures than in TNT–Al and TNT–RDX–Al mixtures. The temperature of the latter will always be in the neighborhood of the final temperature, irrespective of the fraction of explosive reacted, but this is by no means true in fuel sensitized AN mixtures. Two other possible limiting factors besides heat transfer in the condensed phases thus arise. The limiting factor determining rate in the AN–Al mixtures thus might be either (1) mass transfer (or mixing) in the gas phase, or/and (2) heat transfer in the gas phase. In the previous examples studied these processes were apparently unimportant and the rate of reaction was limited by the upper limit of temperature and reaction rate in the solid (the Eyring process). However, in AN–Al mixtures the gaseous phase is apparently not in equilibrium, and factor (1), (2) or both thus limit the rate of reaction. The fact that the rate decreases rapidly with density indicates that the limiting factor is mass transfer. (Diffusion falls rapidly with increasing density or pressure in the vapor phase, but thermal conductivity does not.) This situation corresponds approximately to that occurring in granular "low" explosives such as black powder in which the burning rate decreases with increasing density.

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[9] A. Schmidt, *Z. ges. Schiess und Sprengstoffw.*, numerous articles from 1929 to 1939.

[10] H. Eyring, R. E. Powell, H. H. Duffey and R. B. Parlin, *Chem. Revs.*, **45**, 1 (1949).

Single and double-base propellants in which the solid phase is homogeneous apparently have thermal conductivity as the rate-determining factor. That is, the rate in these explosives is probably determined by the temperature at the solid-vapor interface, but the initial process of decomposition is endothermic or much less exothermic than the over–all reaction. Most of the heat is thus generated a short distance away from solid–vapor interface and must be transferred back by thermal conduction to support the reaction. The temperature gradient away from the surface (temperature being smallest at the solid surface), therefore, increases with pressure, and the effective surface temperature also increases with pressure. The result is that the burning rate increases with pressure.

The anomalous $D(\rho_1)$ curves observed at $d = 10$ cm. in 90/10 AN–DNT are characteristic of nearly all AN-combustible mixtures in small diameter. Quantitative studies of the D/D^* *vs.* ρ_1 curves of such mixtures should thus lead to valuable information on mass transfer in gases at higher densities and pressures in addition to important practical and theoretical information regarding the reaction kinetics of AN-combustible mixtures.

THERMODYNAMIC FUNCTIONS FOR THE SOLUTION OF SILICA IN WATER

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The thermodynamic functions connected with the equilibria between both high surface area, amorphous silica and quartz and aqueous solutions saturated with monosilicic acid (H_4SiO_4) were calculated from data reported in the literature.

Introduction

Although accurate measurements have been made of the solubility of high surface area amorphous silicas[2–5] and quartz[2,4] in water at various temperatures, the thermodynamic functions connected with these equilibria have not yet been reported.

The equilibrium between solid silica and saturated aqueous solutions may be written

$$SiO_2(s) + mH_2O(l) \rightleftarrows H_4SiO_4\cdot aq \qquad (1)$$

Since the silicic acid is very weak[6] no appreciable dissociation in neutral water would be expected. It has been established fairly conclusively that the soluble species of silica in neutral solutions of low ionic strength is monosilicic acid.[2,4] Therefore, the equilibrium constant for the reaction K_c is equal to the activity of the monosilicic acid. Because the concentration of silicic acid in saturated solutions is small, it is possible to equate activity with concentration (moles/l.) without introducing a large error.

Results

Calculation of ΔH, $\Delta F°_{200°}$ and $\Delta S_{200°}$.[7]—Data for the evaluation of these quantities were taken from Iler[2] and Kennedy.[4]

In order to calculate the heat of reaction ΔH for the equilibrium (eq. 1) the van't Hoff equation was used. In Fig. 1 the negative logarithm of the concentration of silicic acid is plotted as a function of the reciprocal of the absolute temperature. ΔH values were determined from the average slopes (Table I).

Table I

Thermodynamic Functions for Solution of Silica

	Amorphous silica	Quartz
ΔH, kcal./mole	$+2.65 \pm 0.28$	$+7.34 \pm 0.37$
$\Delta F°_{200°}$, kcal./mole	$+3.98 \pm 0.04$	$+5.20 \pm 0.04$
$\Delta S_{200°}$, cal./deg. mole	-2.82 ± 0.50	$+4.53 \pm 0.71$

It is obvious from the deviations from the average

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[1] Chemistry Department, Seton Hall University, South Orange, New Jersey.

[2] For review see R. K. Iler, "The Colloid Chemistry of Silica and the Silicates," Cornell University Press, Ithaca, N. Y., 1955.

[3] G. B. Alexander, W. M. Heston and R. K. Iler, This Journal, **58**, 453 (1954).

[4] G. C. Kennedy, *Econ. Geol.*, **45**, 629 (1950).

[5] C. S. Hitchen, *ibid.*, **40**, 361 (1945).

[6] S. A. Greenberg and J. J. Hermans, *J. Phys. Chem.*, in press.

[7] For discussion see F. H. MacDougall, "Physical Chemistry," The Macmillan Co., New York, N. Y., 1936.